Detection of Metallic Mordants on Textiles by Particle-Induced X-Ray Emission

E. T. Williams
Brooklyn College

N. Indictor
Brooklyn College

Follow this and additional works at: https://digitalcommons.usu.edu/electron

Part of the Life Sciences Commons

Recommended Citation
Available at: https://digitalcommons.usu.edu/electron/vol1986/iss3/5

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Electron Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.
DETECTION OF METALLIC MORDANTS ON TEXTILES BY PARTICLE-INDUCED X-RAY EMISSION

E. T. Williams* and N. Indictor

City University of New York
Chemistry Department, Brooklyn College
Brooklyn, N.Y. 11210

(Received for publication February 18, 1986, and in revised form July 22, 1986)

Abstract

A group of modern wool and cotton samples prepared as mordanted standards was subjected to particle-induced x-ray emission analysis (PIXE). The mordants applied were potassium aluminum sulfate, cupric sulfate, ferrous sulfate, stannous chloride, and potassium dichromate. Results agreed with analyses of identical mordanted standards by energy-dispersive x-ray spectrometry in a scanning electron microscope (SEM-EDS).

Key Words: Particle-induced x-ray emission, x-ray, mordants, textiles, metal analysis, cotton, wool.

Introduction

A series of studies performed in the Objects Conservation Department of the Metropolitan Museum of Art, New York, has suggested that energy-dispersive x-ray spectrometry with a scanning-electron microscope (SEM-EDS), serves well for the analysis of metallic mordants on textiles (Koestler et al., 1985a); (Indictor et al., 1985); (Koestler et al., 1985b). The analytical procedure applies also to metal-wrapped yarns (Indictor and Koestler, 1986), metallic salts used to weight fabrics (Ballard et al., 1985), pigments painted on textile (Lee-Whitman and Skelton, 1983), and special dyes which contain elements above fluorine (e.g., shellfish purple, 6,6′dibromoindigo, also known as Tyrian Purple)(Koestler et al., 1985a). In addition, the analysis may be used to characterize accretions on the surface of a textile, indicating evidence for the history of the artifact (Koestler et al., 1985b). If the accretion contains substances with elements heavier than fluorine, these elements will be detected. Substances containing elements lighter than fluorine escape detection. Hence, most organic dyes escape detection; organic mordants or additives (e.g., sumac, tannins, fatty acids, etc.) also escape detection (Indictor et al., 1985).

An alternative analytical procedure, particle-induced x-ray emission (PIXE), is capable of producing the same data with comparable sensitivity and limitations. To test the appropriateness of this analytical procedure, a group of mordanted cotton and wool samples prepared in the Textile Conservation Laboratory of the Metropolitan Museum were subjected to PIXE analysis. The samples were taken from the same fabrics already assayed by SEM-EDS. The results were comparable in each case. The PIXE system can detect the presence of aluminum, but magnesium is difficult because of absorption of the soft x-ray in the detector window. Sodium is not detectable.

Experimental

Materials: Samples of wool and cotton fabric were prepared by the Metropolitan Museum Textile Conservation Laboratory as

---

* Address for correspondence:
  Evan T. Williams
  Department of Chemistry
  Brooklyn College, Brooklyn, N.Y. 11210
  Phone no.: (718) 780-5743
were placed in a modified Kodak Carousel
was necessary except to mount the film on a
with PIXE by comparing the x-ray peak inten­
the Si(Li) detector window. This problem
µm thick polypropylene film by means of one
SnCl2·2H20; potassium dichromate, K2Cr201.
samples of known concentrations. The accu­
those obtained by bombarding reference
35 mm slide card. The targets so prepared
2.5% (wt) solution of polystyrene
dropping one fiber from each sample to a 6.4
PIXE Analysis: Samples were prepared by
x-rays occurs regardless of whether SEM­
SnCl2·2H2O; stannous chloride,
PIXE Analysis: Samples were prepared by
energy-dispersive Si(Li) detec­
and copper were seen in all spectra due to
0.1 mm. A 2 MeV proton has
The chief advantage of PIXE analysis over
SEM-EDS is the ultimate sensitivity which can
Comparing our results with those of
(Koestler et al., 1985a) we note that in the
case of wool samples mordanted with Fe, Sn,
and Cr, a single fiber was insufficient for
the presence of 20 ng of chromium or iron in
the proteinaceous substrate (Stephens, 1975).
The clear sulfur x-ray peak in PIXE analysis of
wool (and presumably silk) may provide an
inherent standard for possible quantitative
mordant determination (and in any case, easy
relative comparisons) as pointed out for
SEM-EDS analysis of dyed wool samples
(Indictor et al., 1985) and historical silks
(Koestler et al., 1985a, 1985b).
Quantitative mordant assay is possible
with PIXE by comparing the x-ray peak inten­
sities in the spectrum of the sample with
those obtained by bombarding reference
samples of known concentrations. The accu­
can be achieved with the former technique. Sensi­
itivity is limited in SEM-EDS by the large
contribution to the background due to electron
bremsstrahlung. The overall intensity of
bremsstrahlung background in PIXE is about one
hundred times less with a corresponding in­
crease in sensitivity compared to SEM-EDS. For
example, it is readily possible to detect the
presence of 20 ng of chromium or iron in
1 mg of wool which yields a sensitivity of 20
ppm.
Comparing our results with those of
(Koestler et al., 1985a) we note that in the
case of wool samples mordanted with Fe, Sn,
and Cr, a single fiber was insufficient for
SEM-EDS analysis but was sufficient for PIXE.
In fact, figure 1 represents the PIXE spec­
trum for a single fiber of wool mordanted
with Fe.

Conclusions
Modern samples of cotton and wool mordan­
ting with potassium aluminum sulfate, ferrous
sulfate, cupric sulfate, stannous chloride, and
copper dichromate were analysed
satisfactorily for Al, Fe, Cu, Sn, and Cr by
references for mordant analysis. Mordanting
procedures have been described (Koestler et
al., 1985a). The mordants used were: potas­
sium aluminum sulfate (alum), K2SO4Al2(SO4)3·
24H2O; cupric sulfate, CuSO4·5H2O; ferrous
sulfate, FeSO4·7H2O; stannous chloride,
SnCl2·2H2O; potassium dichromate, K2Cr2O7.

Results and Discussion
Analysis of the cotton samples showed
clearly the metallic mordants expected in
each case. No evidence of these metals was
seen in the untreated cotton. A trace of
iron and occasionally small amounts of zinc
and copper were seen in all spectra due to
background in the sample chamber.
This background was negligible compared to the
metallic mordants but did set a limit on the
ultimate sensitivity for these elements.
Similarly, PIXE analysis of the wool
samples detected the presence of the expect­
ed metallic mordants in the standard samples.
A major difference in this sample set was the
common presence of a sulfur peak, absent in
cotton. This peak is prominent in wool
due to the cystein and methionine links in
the proteinaceous substrate (Stephens, 1975).

A textile fiber is a rather open material
energy, mass, and charge as well as density
and atomic mass of the material traversed.
The external-beam PIXE system at Brooklyn
College has been described elsewhere in
detail (Williams et al., 1981) (Bauman et
al., 1979). Analysis of each sample re­
quired less than five minutes. Samples
can easily be stored for later reanalysis
if desired, since the analysis is non­
destructive. Samples are not coated as is
required in SEM analysis. A representative
spectrum is shown in figure 1.

Analysis of the cotton samples showed
clearly the metallic mordants expected in
each case. No evidence of these metals was
seen in the untreated cotton. A trace of
iron and occasionally small amounts of zinc
and copper were seen in all spectra due to
background in the sample chamber.
This background was negligible compared to the
metallic mordants but did set a limit on the
ultimate sensitivity for these elements.
Similarly, PIXE analysis of the wool
samples detected the presence of the expect­
ed metallic mordants in the standard samples.
A major difference in this sample set was the
common presence of a sulfur peak, absent in
cotton. This peak is prominent in wool
due to the cystein and methionine links in
the proteinaceous substrate (Stephens, 1975).

The clear sulfur x-ray peak in PIXE analysis of
wool (and presumably silk) may provide an
inherent standard for possible quantitative
mordant determination (and in any case, easy
relative comparisons) as pointed out for
SEM-EDS analysis of dyed wool samples
(Indictor et al., 1985) and historical silks
(Koestler et al., 1985a, 1985b).

Quantitative mordant assay is possible
with PIXE by comparing the x-ray peak inten­
sities in the spectrum of the sample with
those obtained by bombarding reference
samples of known concentrations. The accu­
curacy of the analysis is less for the light­
est elements because of absorption of the
soft x-rays in the fibers themselves and in
the Si(Li) detector window. This problem
is important for aluminum and sulfur but
much less so for elements of higher atomic
number. Sample self-absorption of soft
x-rays occurs regardless of whether SEM­
EDS or PIXE is used. Thus, absolute
analysis is difficult by any energy-dis­
persive method.

Small portions of the reference samples
have been subjected to analysis by atomic
absorption (Koestler et al., 1985a)
(Indictor et al., 1985). The results of
such analysis could be used to calibrate
the PIXE system. In principle, it is
necessary to calibrate all quantitative
results of this type with an independent
method of analysis because a major portion
of the sample (elements of atomic number
< 13) escapes detection. Effects of sample
self-absorption etc. would then be account­
ed for assuming that other fibers subject
to analysis have roughly the same physical
characteristics.

In evaluating PIXE or SEM-EDS methods
of analysis, the question of surface ver­
sus bulk inclusion of mordants in the
fibers in the analytical process arises.
The penetrating range of protons or elec­
trons in matter is a function of particle
energy, mass, and charge as well as density
and atomic mass of the material traversed.
A textile fiber is a rather open material
and exact calculation of the penetration
depth of particles is difficult. The
linear range of a 2 MeV proton in solid
carbon is about 0.1 mm. A 2 MeV proton has
roughly the same penetrating power as a 100­
keV electron so that SEM-EDS systems employ­
ing such electrons have comparable penetra­
tion of the bulk of the samples.

The chief advantage of PIXE analysis over
SEM-EDS is the ultimate sensitivity which can
be achieved with the former technique. Sensi­
tivity is limited in SEM-EDS by the large
contribution to the background due to electron
bremsstrahlung. The overall intensity of
bremsstrahlung background in PIXE is about one
hundred times less with a corresponding in­
crease in sensitivity compared to SEM-EDS.
For example, it is readily possible to detect the
presence of 20 ng of chromium or iron in
1 mg of wool which yields a sensitivity of 20
ppm.

Comparing our results with those of
(Koestler et al., 1985a) we note that in the
case of wool samples mordanted with Fe, Sn,
and Cr, a single fiber was insufficient for
SEM-EDS analysis but was sufficient for PIXE.
In fact, figure 1 represents the PIXE spec­
trum for a single fiber of wool mordanted
with Fe.
PIXE analysis of metallic mordants

fig. 1. PIXE spectrum of single wool fiber mordanted with Fe.

PIXE. The persistent observation of trace metals even for samples not treated with mordant indicates the importance of background scans for these analyses. The clear presence of sulfur in PIXE analysis of wool suggests the possibility of its use as an internal standard in quantitative estimates of metallic mordants or related material on proteinaceous fibers.

Acknowledgements

We are indebted to Nobuko Kajitani of the Textile Conservation Department of the Metropolitan Museum of Art, New York, for supplying samples, and to Gardy Cadet and Noel Guardala for assistance in the PIXE analysis.

References


Discussion With Reviewers

H. Blank: It would help the reader if the authors would differentiate between the techniques which produce the electron-shell vacancies (i.e., protons for PIXE and electrons in an electron microscope) and the energy-dispersive spectrometer (EDS) which is used in both cases for the analysis of the x-rays.

Authors: We agree. The term EDS has been often used in the world of scanning electron microscopists. As EDS is also used in PIXE and x-ray fluorescence, it is clear that a new acronym is needed. Since electron-induced x-ray emission does not yield a "good" acronym (EIXE) we have decided, for the purpose of clarity in this paper, to use SEM-EDS to denote energy-dispersive x-ray spectrometry in a scanning electron microscope (instead of EDS).

H. Blank: Did you find inhomogeneity in your samples, and could you observe beam damage of your samples with PIXE? What accuracy do you expect from PIXE analysis?

Authors: The fiber samples were about 1 mm diameter by 3 mm long. The beam spot had a 1 cm diameter so that the result referred to the entire fiber. No beam damage was observed. The He atmosphere allows for cooling of the sample. Quantitative analysis by PIXE is generally accurate to 5-10 percent on a routine basis with better accuracy possible if stringent precautions are taken. 

849
Reviewer III: What are the comparative advantages of PIXE (in the case of analyzing textile fibers) over x-ray fluorescence (XRF) as well as SEM-EDS?
Authors: The chief advantage of PIXE over XRF for textile fiber analysis is that a single fiber is too small for conventional XRF but not for PIXE.

J.R. Chen: What was the range of sulfur concentrations in the wool samples and would large variations negate the use of sulfur as an internal standard?
Authors: Inasmuch as this was a feasibility study, qualitative rather than quantitative analysis was performed. The fibers were not weighed. There did not appear to be large variations in sulfur content in the six wool samples analyzed. Use of sulfur as an internal standard, however, is not yet established as it is known that sulfur can be lost as the fibers age and the sulfur content may change depending on how the textile is handled over the course of time. Further research would be required.

H. Blank: A wavelength-dispersive spectrometer is more sensitive due to better peak-to-background ratio. Did you carry out investigations of your samples with an electron microprobe?
Authors: No, we did not use wavelength-dispersive analysis.